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AN INVESTIGATION OF THE DEGRADATION OF PROPYLENE CARBONATE
BY CHLORINE

Suen-Man G. Yu, Philip N. Ross, and Charles W. Tobias
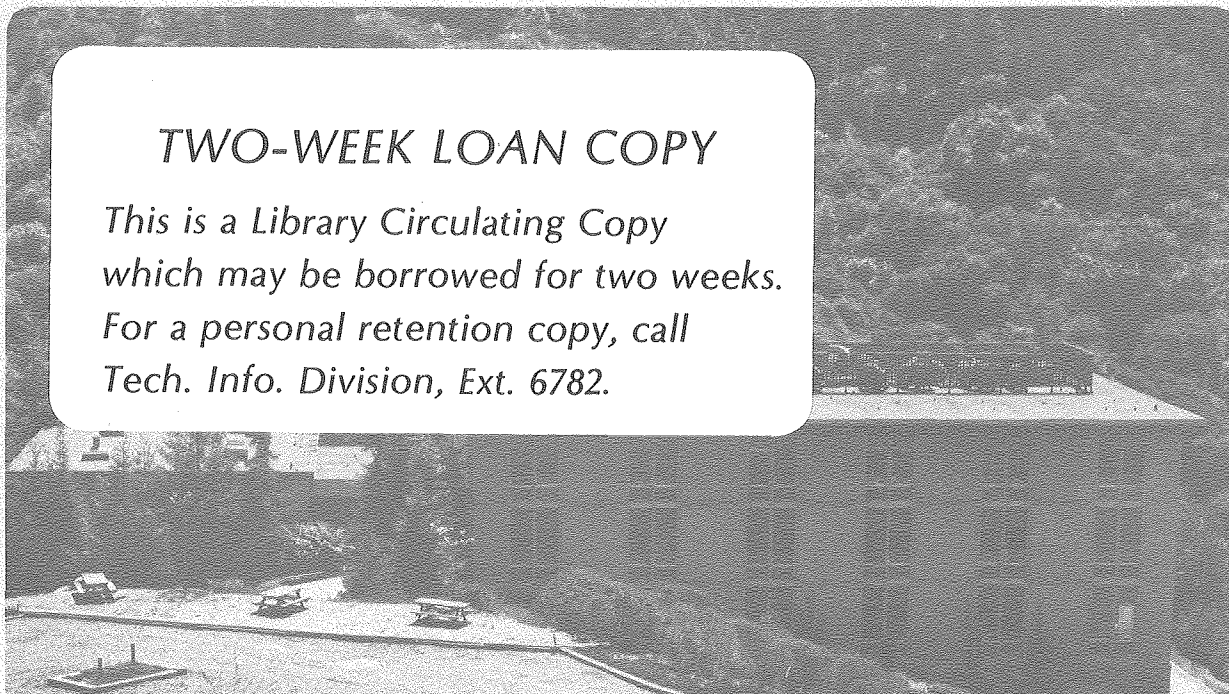
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An Investigation of the Degradation of Propylene Carbonate
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ABSTRACT

Chlorine was found to degrade a very carefully purified propylene
carbonate solvent. Water present in the solvent at a few parts per
million level is identified to be the cause of the degradation. It is
shown that water not only affects the rate, but also the extent of the
degradation. An order of magnitude estimate indicates that 10 ppm of water
causes a tenfold increase in both the rate and the extent of the degrada-
tion. Treated Nafion membrane was found to be adequate for confining
chlorine evolution and hence solvent degradation to only the anodic chamber.
Potassium was simultaneously deposited in the cathodic chamber where no
solvent degradation was observed. The chlorine evolution potential of a
0.5M $KAlCl_4$ in propylene carbonate relative to a potassium reference
electrode was determined by voltammetry to be 3.5 volts.

Introduction

Although it is one of the most abundant elements in the world, metallic potassium is not widely employed in chemical technology. It is used in a number of organic synthesis reactions, and as a heat transfer fluid in certain nuclear reactors. It is also used in the manufacture of potassium super-oxide, KO_2, which serves as an oxygen source in gas mask applications.

Currently potassium is produced from an exchange reaction with sodium metal. The process is thermochemical (J2), see Figure 1, and is extremely energy intensive. The potassium produced has a considerable amount of impurities, notably sodium. Unlike other common alkali metals, potassium is not produced electrochemically (S1). This is because potassium has a high vapor pressure at cell-operating temperature causing undesirable metal mist formation. Also, potassium is an extremely corrosive metal. Worst still, it is potentially explosive upon contacting with air or oxygen.

In the past, we have investigated the possibilities of producing potassium electrochemically in our laboratory. All of our works were centered on searching for and using an organic solvent which is capable of ionizing inorganic salts. Aqueous solvent is not used because of thermo-dynamic limitation.

As early as 1958, Harris and Tobias (H1) had successfully obtained electrochemically deposited alkali metals using various organic solvents and inorganic salts. Jorne (J3) in 1972 concluded a study regarding the electrochemical behaviour of alkali metals in propylene carbonate solvent. The propylene carbonate solvent was subsequently chosen to be the solvent for further study. Recently, Law (L1) has studied extensively potassium
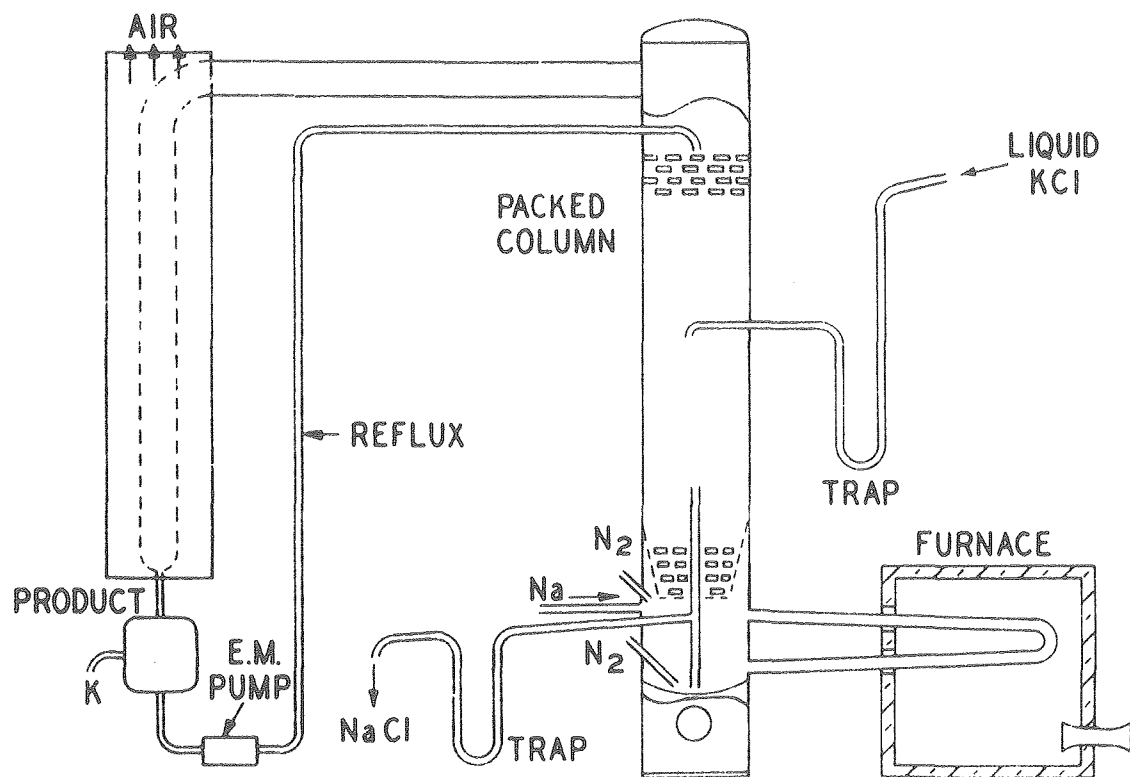
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Figure 1. Continuous process for potassium production.

deposition in propylene carbonate. He established the feasibility of the process for primary recovering and/or refining of potassium metal from an inorganic double salt, potassium tetrachlorate aluminate ($KAlCl_4$), in propylene carbonate using either potassium or aluminum anodes. Future study will be in the direction of identifying new anodic reactions which are compatible with the potassium reduction reaction at the cathode. One such candidate would be the anodic chlorine evolution using the $KAlCl_4$/propylene carbonate electrolytes. It is thus the aim of this study to determine the compatibility of the propylene carbonate solvent with respect to chlorine. The electrolyte chosen for this study is $KAlCl_4$ in propylene carbonate.

Experimental Procedure

A. Glove Box Operation

Because of the ease of atmospheric contamination of the electrolysis system, experiments were primarily conducted in a glove box filled with dry helium. It was essentially the same glove box used by Law (L1) in his study.

The glove box was a vacuum type of Lawrence Livermore design. It was used previously by both Jorne and Law in their research investigations. The helium in the glove box was continuously recirculated through an inert gas purifier (Kewaunee Scientific Equipment Model 2c1982) which removed both oxygen and moisture from the helium. The purifier was regenerated periodically by passing heated gaseous mixtures of hydrogen and helium

through it. The moisture level in the helium was monitored (Moisture Monitor, Consolidated Electrodynamics Corporation Model 26-303ME) and maintained at or below 2 ppm.

The glove box was equipped with an entrance chamber and two glove ports. All materials transferred in and out of the box went through the entrance chamber in which vacuum as low as 10 millitorr could be imposed to ensure effective removal of moisture and other potential contaminants. The glove ports, when not in use, were bolted and evacuated. This ensured minimal gas diffusion through the gloves.

The glove box was also equipped with an electronic balance (Scientech Model 220), an outside house vacuum source (60 mm Hg), and a temperature monitor (Omega Engineering Model MCJ-T) which continuously monitored the temperature of the glove box.

B. Solvent Purification

The propylene carbonate solvent as received (Jefferson Chemical Company, Texas) (J4) contained a few percent of impurities. The major impurities were water, propylene oxide, propylene glycols, allyl alcohol, and propionaldehyde, etc. Gas chromatography was used to detect and analyse these impurities. A quantitative breakdown of these impurities is given in Table 1. The solvent has a characteristic light yellowish color possibly due to the polymerised product of the impurities.

The solvent was purified by means of an absorption column and a vacuum distillation unit. A flow diagram of the purification steps and a picture of the apparatus is shown in Figures 2 and 3, respectively.

Table 1. Impurities in the As-Received Propylene Carbonate Solvent

Impurity	Level (ppm)	Structure
Water	10^3-10^4	H_2O
1,2 and 1,3 Propylene glycol	$\sim 2\times 10^4$	(1,2) CH_3-CH-CH_2 with OH OH (1,3) CH_2-CH_2-CH_2 with OH OH
Propylene oxide	500	CH_3-CH-CH_2 with O
Allyl alcohol	200	H_2C=CH-CH_2-OH
Propionaldehyde	200	CH_3-CH_2-$\overset{H}{C}$=O
Formaldehyde	<100	HCHO
Acetone	<100	$CH_3\overset{O}{\overset{\|}{C}}CH_3$
CO_2	v. small	CO_2
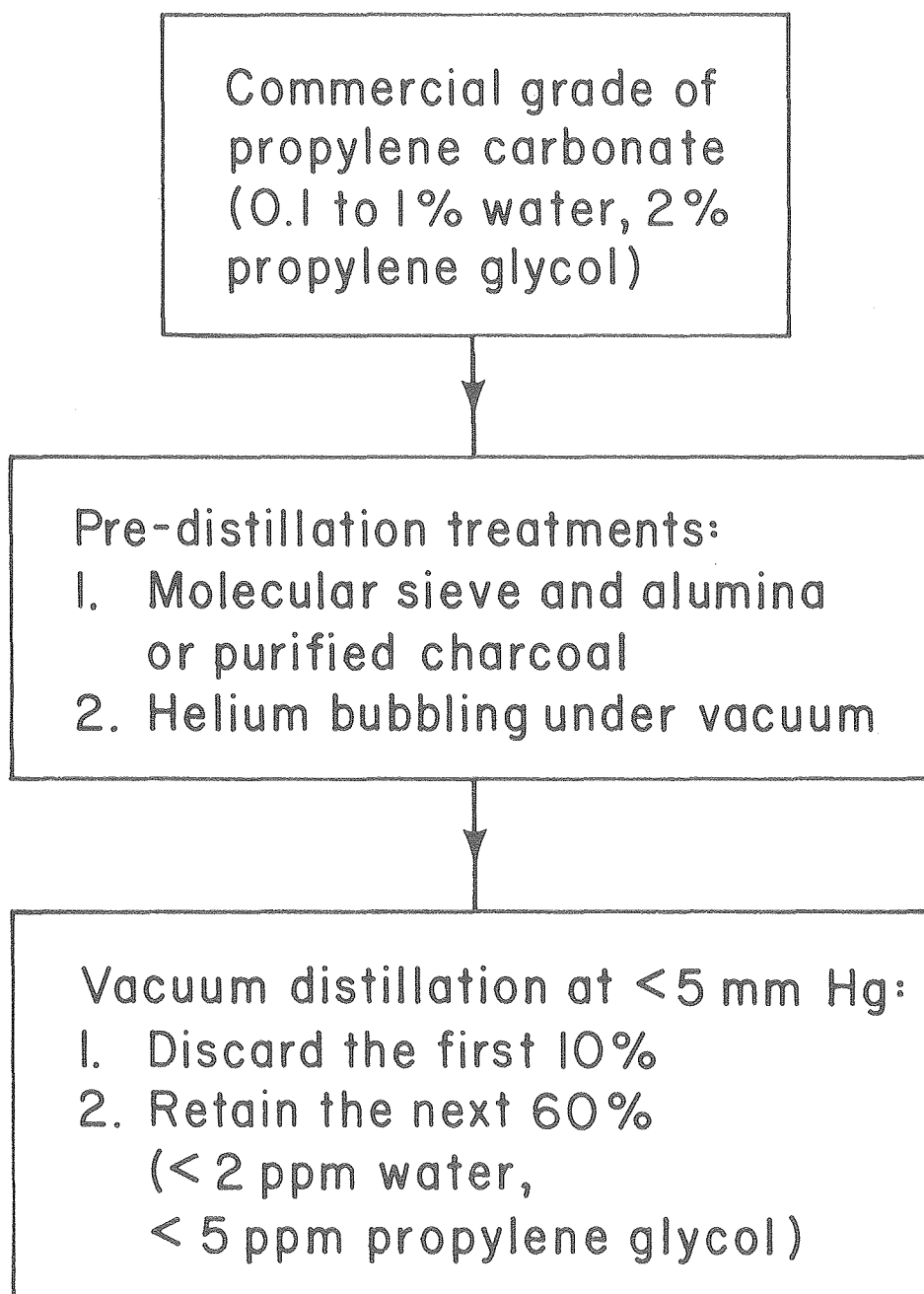
Figure 2. Flow diagram for the purification of propylene carbonate.
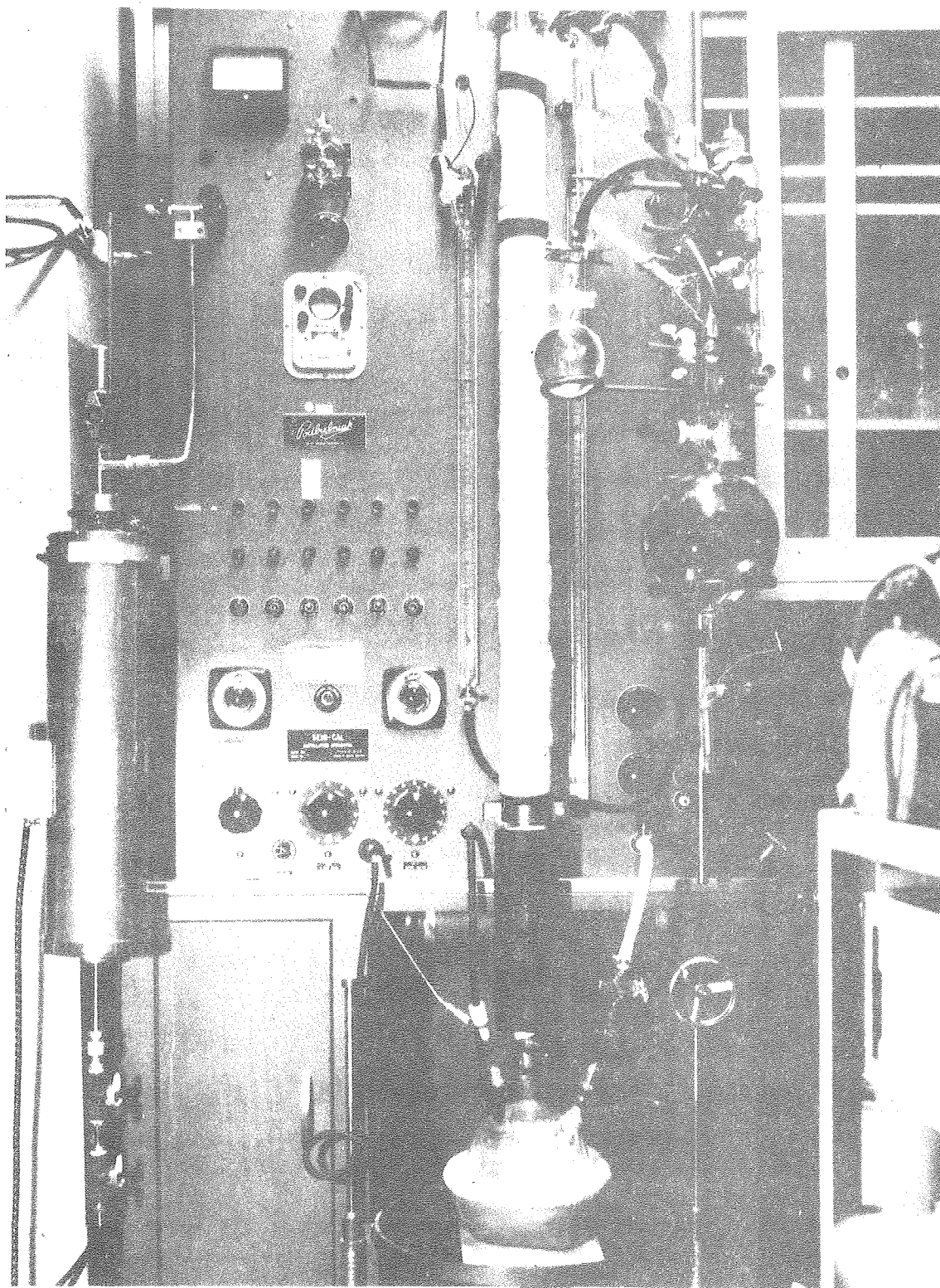
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Figure 3.   The propylene carbonate solvent purification apparatus.

The absorption apparatus is located to the left of the distillation column.

The absorption column (600 ml capacity) was packed with an equal mixture of molecular sieve (Linde type 13X) and vacuum-dried aluminum oxide. They were chosen and proved to be good absorbents for solvent pretreatment steps to remove most of the impurities, especially water. The pretreated propylene carbonate solvent was then vacuum distilled (Semi-Cal Series 3650, Podbielniak, Dresser Industries) at a pressure of less than 5 mm Hg and a head temperature of no more than 65°C. The first 10% and the last 30% were discarded. Only the middle fraction was retained for electrochemical study. Vacuum distillation was employed to eliminate and/or minimize the possibility of thermally decomposing the product. Prior to the distillation, helium was bubbled through the pretreated propylene carbonate solvent overnight. This was meant to remove the light volatile impurities in the solvent. The boiling was carefully controlled by bubbling helium at a very slow rate (3-5 bubbles per second). This ensured a "smooth" boiling and helped to remove the impurities. The pretreated and distilled propylene carbonate were analytically determined to have < 2 ppm of water and < 5 ppm of propylene glycol.

C. Gas Chromatographic Analysis

Because of the sensitivity of potassium towards impurities in the solvent, the ability to monitor solvent impurities especially water and propylene glycol down to ppm levels is essential. Gas chromatography (GC, Varian Model 3760) was exclusively employed for this purpose.

The GC was equipped with dual columns connected to either thermal or flame ionization detectors. The operating conditions of the GC are depicted in Table 2. Essentially, we have chosen the same operating conditions used by Jasinski and Kirkland (J5). Typical chromatogramms of a treated and untreated propylene carbonate are shown in Figure 4.
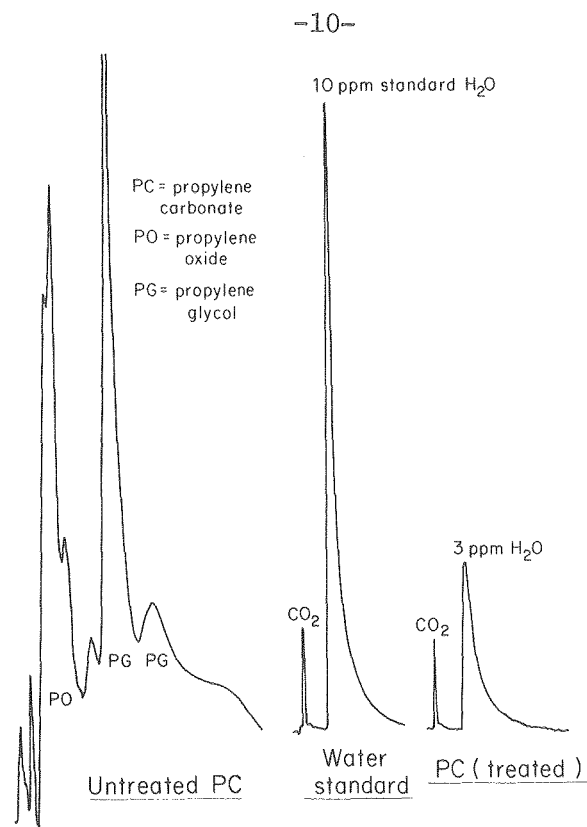
Table 2. Gas Chromatograph Operating Conditions

	Gas Flow (mℓ/min)			Temperature (°C)			
	He	H$_2$	Air	Injectors	Column	Detector	Filament
Flame Ionization Detector	30	30	300	150	150	200	—
Thermal Conductivity Detector	60	—	—	150	150	200	300

The treated solvent was estimated to have residual impurities of no more than 2 ppm and 5 ppm of water and propylene glycol, respectively. The estimation was made by comparing peak area against standards. Standards were made up by incorporating known amounts of impurities into the treated solvent. For all practical purposes, linear behavior was assumed for the sake of simple comparison.

D. Salt Preparation

The salt used in this study is potassium tetrachloro aluminate (KAlCl$_4$). It is not available commercially. It was synthesized in our laboratory by the following procedure:

10 ppm standard H_2O

PC = propylene
carbonate

PO = propylene
oxide

PG = propylene
glycol

3 ppm H_2O

CO_2

CO_2

PG PG

PO

Untreated PC

Water
standard

PC (treated)

XBL 799-4256

10 ppm

<1 ppm
PG

CO_2

CO_2

PC (treated)

PG standard
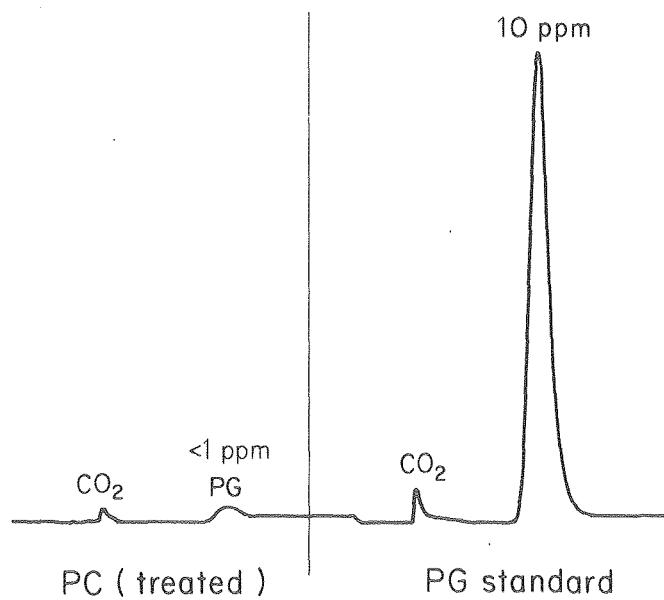
XBL 799-4257A
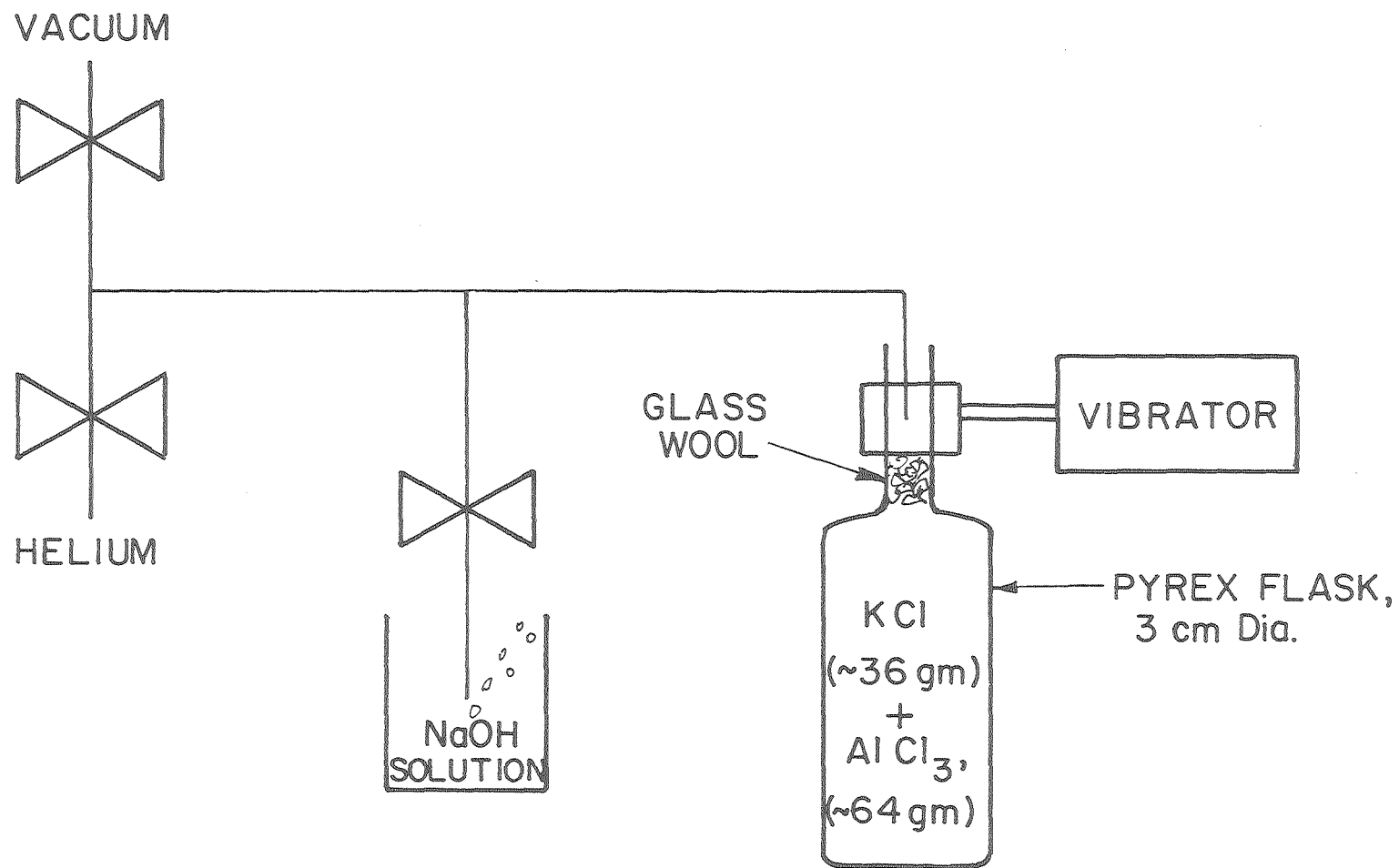
Figure 4.   Chromatogramm of treated and untreated propylene carbonate.

Equal molar amounts of aluminum chloride ($AlCl_3$) and potassium chloride (KCl) were first weighed and then mixed into a pyrex tube under inert nitrogen atmosphere. A polyethylene glove bag (Instruments for Research and Industry, Cheltenham, Pennsylvania) was used for this purpose. The tube was then evacuated overnight, as shown in Figure 5, to below 3 mm Hg; the contents were kept thoroughly mixed by a vibrator. The tube was then filled and continuously bled with helium while it was immersed into an oven which was slowly heated up to 550°C. The salt in the tube was melted and the subsequent solution was clear and colorless. Black precipitate was observed in the bottom of the tube after about 2 hours. The salt solution was then slowly cooled. It recrystallised in the form of white crystals. The tube was subsequently sealed and transferred quickly into the glove box. Once inside the glove box the tube was cracked open. The salts were ground to fine powder ready for use.

E. Cell Configurations/Electrolysis Cells

There are basically three cell configurations in this study. They are depicted in Figures 6 through 8.

Cell #1 (Figure 6) was used in preliminary investigations. Chlorine gas was passed into a precision sampling bottle through a series of tubing and bleed valves. It bubbled at a rate of roughly 1 ml/min. (about 3-5 bubbles per second) through the propylene carbonate solution in the cell. Samples were withdrawn by syringe through a rubber septum which provided a good seal for the contents in the cell. The once-through chlorine was bled off through a side valve into a flask/beaker containing sodium

VACUUM

HELIUM

GLASS
WOOL

VIBRATOR

NaOH
SOLUTION

KCl
(~36 gm)
+
AlCl$_3$,
(~64 gm)

PYREX FLASK,
3 cm Dia.

XBL 793-5969

Figure 5.   Schematic for the synthesis of KAlCl$_4$.

⊠ : Needle valve

Precision Sampling Bottle
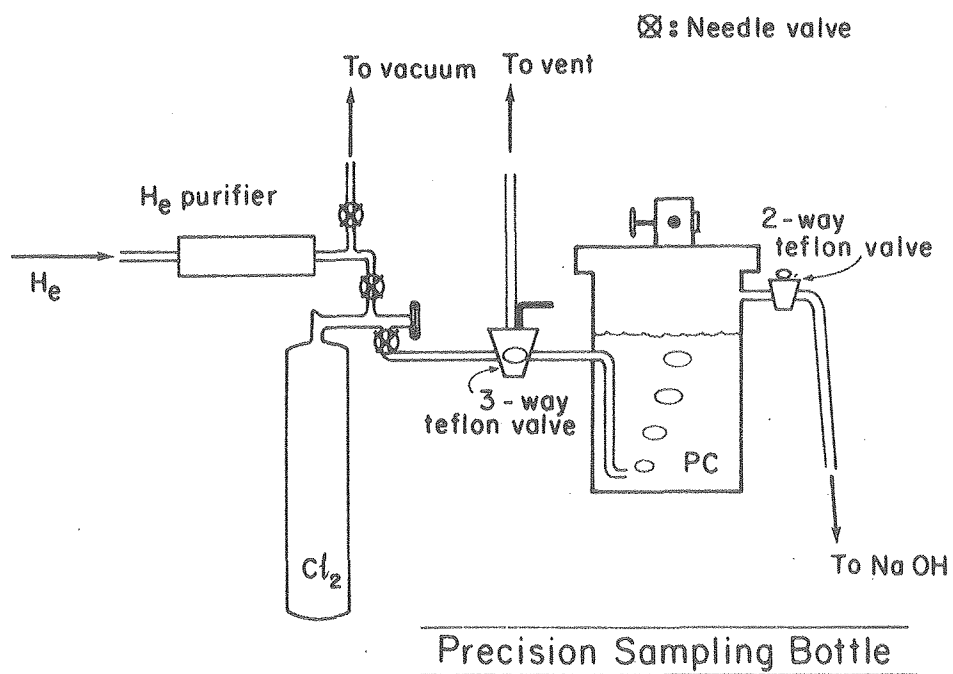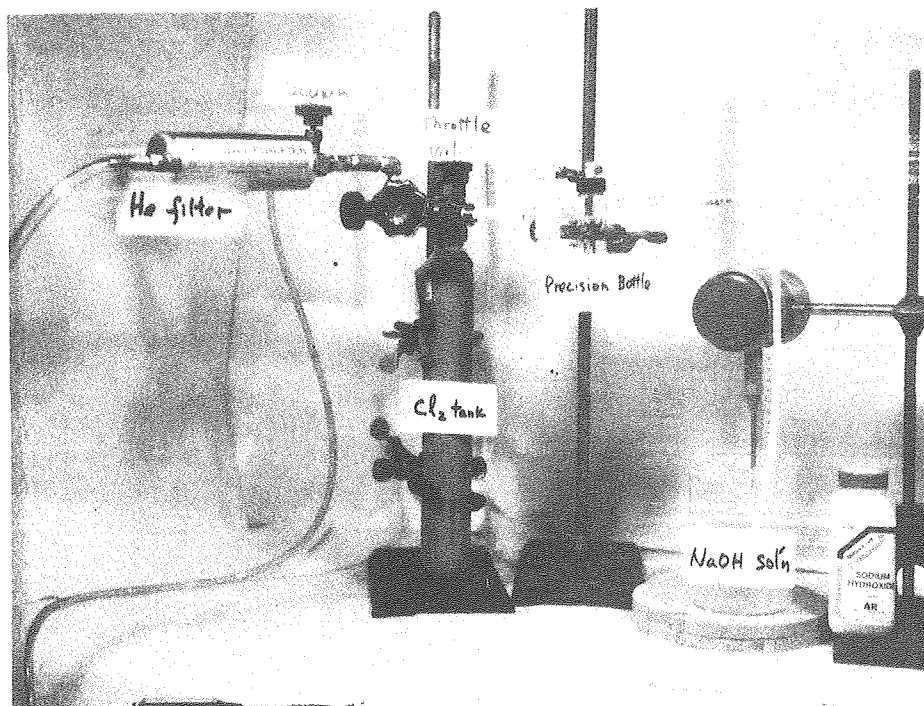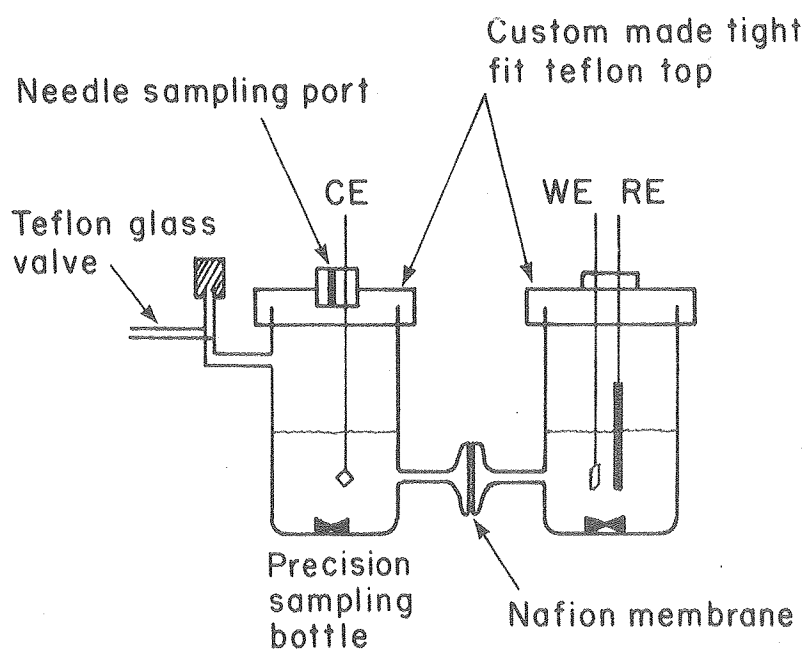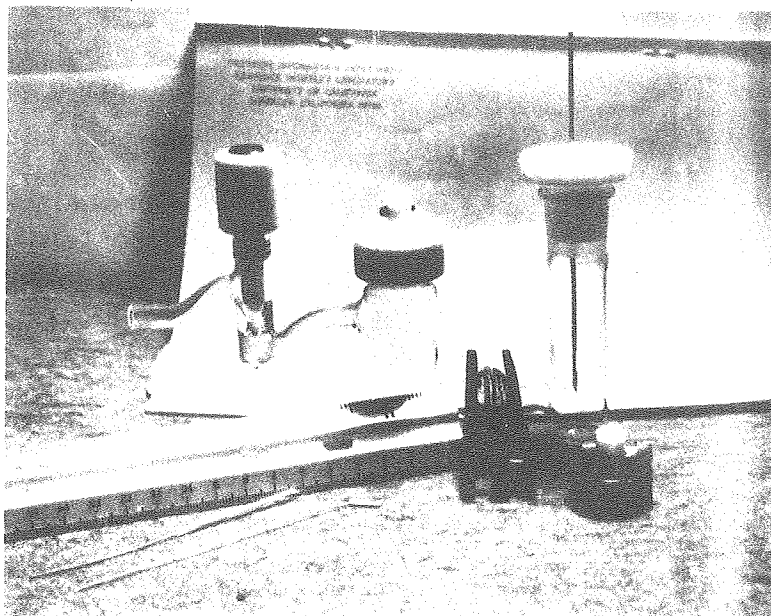
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Figure 6. Cell (#1) configuration for the Cl_2/PC stability study.
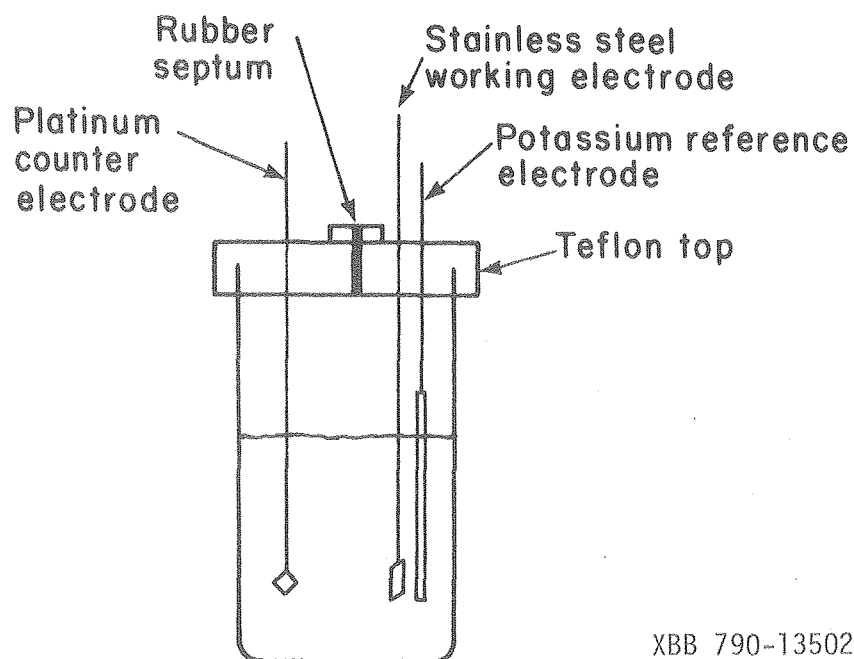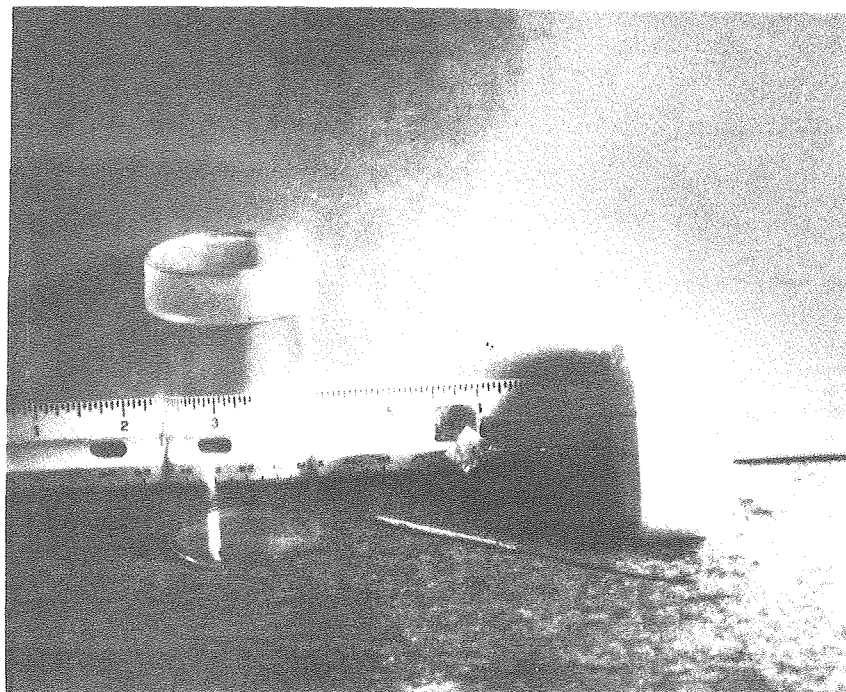
Figure 7. Cell (#2) configuration for the Cl_2/PC stability study.

Figure 8. Cell (#3) configuration for the Cl_2/PC stability study.

hydroxide.

The #2 cell (Figure 7) consisted of a 75 ml flask and a specially custom made teflon top equipped with a small rubber septum. Electrolysis was carried out with all three electrodes, the working, counter and reference electrodes (stainless steel, platinum and potassium, respectively) immersed in the same cell. Both working and counter electrodes are 1 cm^2 in cross-sectional area.

The #3 cell (Figure 8) was based on the H-cell design concept. The anodic chamber housing the counter electrode was separated from the cathodic chamber by a Nafion membrane (Dupont's Nafion #425). The membrane was treated with potassium hydroxide, double distilled water and then thoroughly dried before use. During electrolysis, chlorine evolved only in the anodic chamber. The electrodes, which are of 1 cm^2 in area, were made of the same material as in cell #2.

Process Description

Propylene carbonate, an organic cyclic ester, is a dipolar aprotic solvent. It has a high dielectric constant, a low melting point and a high boiling point. The solvent is capable of ionizing many inorganic salts. It is this unique property that has enabled us to utilize it in our electrochemical study. Other desirable characteristics of the solvent are that it is non-toxic, non-corrosive and capable of withstanding a relatively high potential without decomposition. The structure and some basic properties of propylene carbonate are depicted in Table 3.

The process used to study the stability of the solvent with respect to chlorine evolution was the electrolysis of $KAlCl_4$ in propylene

Table 3. PHYSICAL PROPERTIES OF PROPYLENE CARBONATE(PC)

Structure	$CH_3\!-\!CH\!-\!CH_2$ with O, O bonded to C and $C\!=\!O$
Molecular Weight	102.09
Melting Point, °C	-49.2
Boiling Point at 760 mm Hg, °C	241.7
Vapor Pressure at 25 °C, mm Hg	0.069
at 60 °C, mm Hg	0.80
Density at 25 °C, gm/cm^3	1.203
at 60 °C, gm/cm^3	1.161
Viscosity at 25 °C, millipoises	24.8
at 60 °C, millipoises	13.3
Dielectric Constant at Room Temperature	65.1
Specific Conductance at 25 °C, ohm^{-1}cm^{-1}	1.2 to 8.6 x 10^{-7}
at 60 °C, ohm^{-1}cm^{-1}	1.5 to 10.0 x 10^{-7}

From R. Keller et al., Properties of nonaqueous electrolytes, NASA CR-1425, 1969.

XBL 7712-11291

carbonate. Chlorine was produced and evolved at the anode. Potassium was reduced or deposited at the cathode. The overall reaction involved is

$$KAlCl_4 \rightleftharpoons K^+ + Cl^- + AlCl_3$$
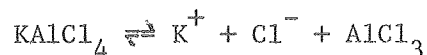
The half reactions at the cathode and anode are, respectively:

$$K^+ + e^- \rightarrow K$$

and

$$Cl^- + Cl^- \rightarrow Cl_2 + 2e^-$$
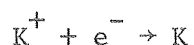
Assuming a 100% current efficiency, two moles of potassium were deposited for every mole of chlorine evolved.

This proposed chlorine evolution anodic reaction was quite attractive from the point of view of raw material considerations. Theoretically only KCl is consumed in the electrolysis. It can be replenished by simply adding KCl into the system. Hence this process is capable of producing valuable chemicals, potassium and chlorine, from a relatively cheap source, KCl. The most important consideration of all, however, is that the system can be operated at room temperature.

RESULTS AND DISCUSSION

A preliminary stability study was performed using cell #1 (Figure 6) where chlorine was introduced/bubbled into a precision sampling bottle. The bottle allowed samples to be withdrawn by a syringe through a tightly fitted rubber septum. The bottle was first charged with approximately

15 ml. of purified propylene carbonate inside the glove box. The
propylene carbonate was analytically determined to have <2 ppm of water
and <5 ppm of propylene glycol. The bottle was then taken out of the glove
box and connected to a three way valve which directed and controlled
helium and chlorine flow. The whole system was flushed and reflushed
several times with dry treated/filtered helium prior to chlorine bubbling.
Samples were taken both before and after helium and chlorine bubbling.
The rate of bubbling was estimated to be 3-5 bubbles per second, which
is roughly equivalent to 1-1.5 ml. per minute. The result of this
experiment is shown in Table 4.

During the initial phase of the bubbling, the solution turned pale
yellowish green. However, it turned more and more yellowish as more
chlorine passed into the solution. The preliminary conclusion drawn from
the result of this experiment is that chlorine does degrade even the most
carefully purified propylene carbonate. Judging from the analysis of
the solvent after helium flushing, atmospheric contamination was believed
to be negligible if not completely eliminated. It was also observed that
the degradation was quite rapid and appeared to arrest after 2 hours.
At this point, a 1 μl of PC containing 10 ppm water was injected into the
solution in the precision bottle while chlorine continued to bubble. A
sample was taken at about 30 min. after the injection. The sample was
again analysed by gas chromatography. The result is indicated in the
last column in Table 4. It shows that addition of 10 ppm of water at
this later stage did not cause any further PC degradation.

Looking at these results, even though water addition did not cause

Table 4. Analytical Results of Bubbling Cl_2 Through Propylene Carbonate Using Cell #1

	Before He flush	After He flush	Cl_2 Bubbling					After 10 ppm of water was injected into the bottle
			30 sec.	15 min.	1 hour	2 hours	>2 hours	
Propylene oxide	0	0	239	10^3	3×10^4	5×10^4	5×10^4	5×10^4
Propylene glycol	<5	<5	200	10^3	2×10^4	5×10^4	slightly more than 5×10^4	$\sim5\times10^4$
Allyl alcohol	0	0	98	5×10^2	10^3	10^3	10^3	10^3
Acetone/ Propionaldehyde	0	0	113	5×10^2	10^3	10^3	10^3	10^3
Water	<2	<2	–	<2	–	<2	<2	~10

further solvent degradation, it appears likely that water activates

and participates in the degradation of propylene carbonate. A pre-

liminary degradation scheme shown in Figure 9 may be proposed. While

proving this scheme is beyond the scope of this study, propylene

carbonate is conceivably degradable to products so far identified via

GC.

A similar experiment, with addition of 10 ppm of water before

chlorine bubbling was conducted to study the effect of water on the

degradation of propylene carbonate. Samples were again taken at

various time intervals. The results are tabulated in Table 5.

The water is shown not only to affect the extent of propylene

carbonate degradation but also the rate of degradation. An addition of

10 ppm of water causes the rate of degradation to increase by almost

tenfold. This further confirms the observation that water has initiated

and participated in the propylene carbonate degradation.

The resultant propylene carbonate/chlorine solution was flushed with

helium which gradually decolorized the solution and eventually turned it

into a slightly yellowish solution. Samples were taken and analyzed

by Infrared Spectroscopy for chlorinated compounds. The result showed

that the decolorized solvent was not chlorinated. This indicates that

the degradation mechanism apparently does not involve chlorination steps

and that pure/dry propylene carbonate solvent could be inert towards

dry chlorine.

The second stage of this investigation/study was to produce

chlorine in-situ in an electrochemical cell (#2) shown in Figure 7.

Fifty ml. of purified propylene carbonate was added into this cell inside

Degradation Mechanism
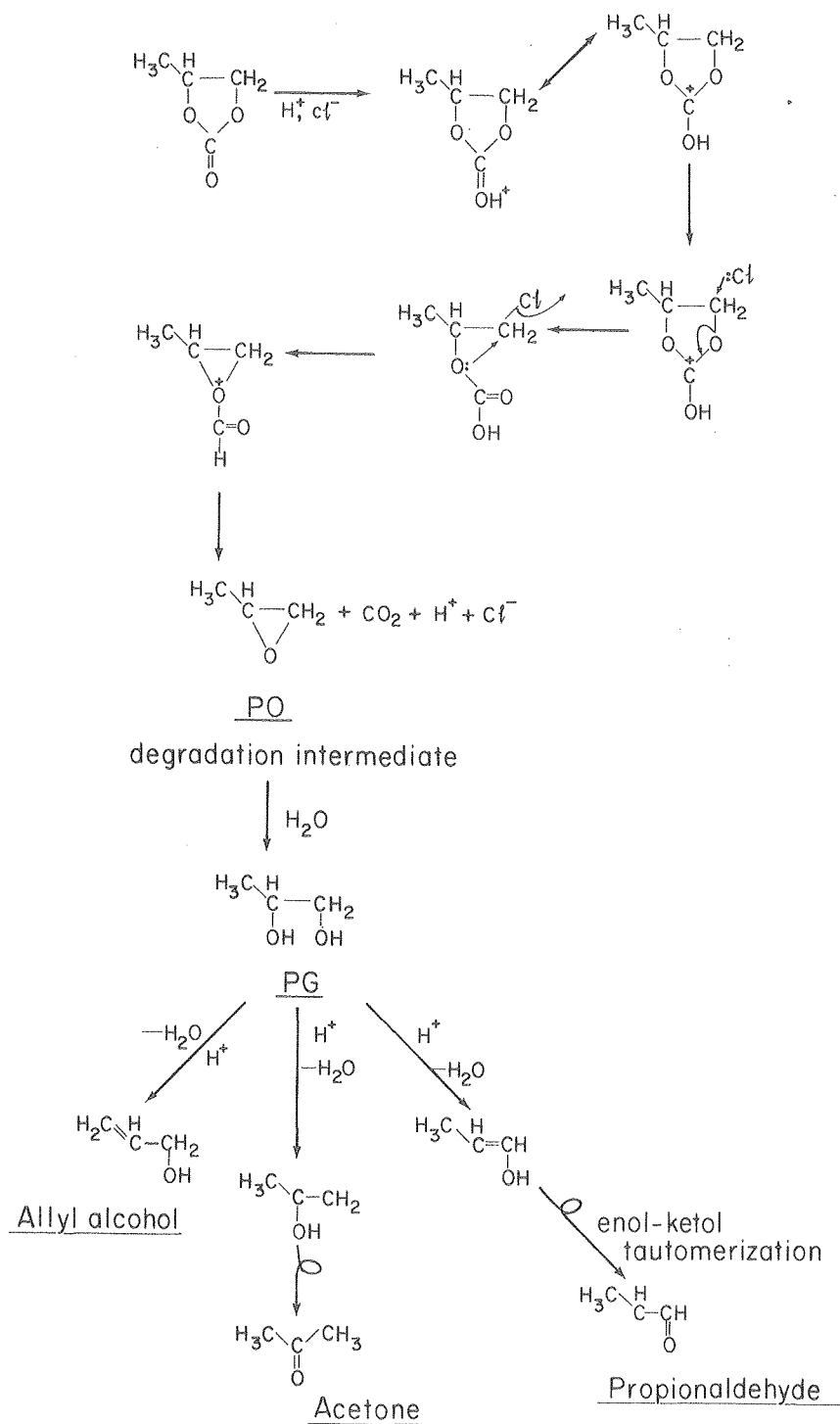
Figure 9. Proposed mechanism for propylene carbonate degradation.

Table 5. Effect of 10 ppm of Water on Propylene Carbonate Degradation

(ppm)

	Initial	After Cl_2 Bubbling				
		30 sec	18 min	1 hr	2 hr	>2 hr
Propylene oxide	0	2000	10^4	7×10^4	10^5	10^5
Propylene glycol	<5	3300	10^4	10^5	10^5	10^5
Allyl alcohol	0	137	5×10^2	10^3	10^3	10^3
Acetone/Propionaldehyde	0	325	10^3	10^3	10^3	10^3
Water	∿10	--	10	--	10	10

the glove box. A potential of 3.5 volts was applied through a
potentiostat (PAR Model 173) to the stainless steel working
electrode and the platinum counter electrode. A potassium electrode
was used as a reference electrode. The chlorine evolution poten-
tial of 3.5 volts was established previously by the use of cyclic volta-
mmetry technique (Figure 10). An initial current density of 8 ma/cm^2 was
obtained. It slowly increased to about 15 ma/cm^2 after about 2 hours. The
potassium deposit started to appear after about 5 minutes; the solution
gradually turned yellowish. The deposits were dark grey in color and
adhered loosely to the working electrode. They were easily shaken off by
slight agitation. Two 2 µl samples were withdrawn at less than 1 min.,
and 2 hours interval for GC analysis. The result is shown in Table 6.

To study the effect of water on already degraded propylene carbonate,
10 ppm of water was injected into the solution. Electrolysis was carried
out further using the same condition. A sample was again taken approxi-
mately an hour later. The results, tabulated in the last column of Table 6,
indicate that propylene carbonate was further degraded. This contrasts
with the earlier results, although in this case further degradation
occurred with simultaneous potassium deposition. The results of these
three experiments clearly indicate that water was responsible if not the
only reason for solvent degradation.

An H-cell (#3--Figure 8) was used in the third stage of this study. The
anodic and cathodic chambers were separated by a Nafion membrane. Thirty ml.
of purified propylene carbonate was added into the cell inside the glove
box. A volage of 3.5 volts was again imposed between the working and
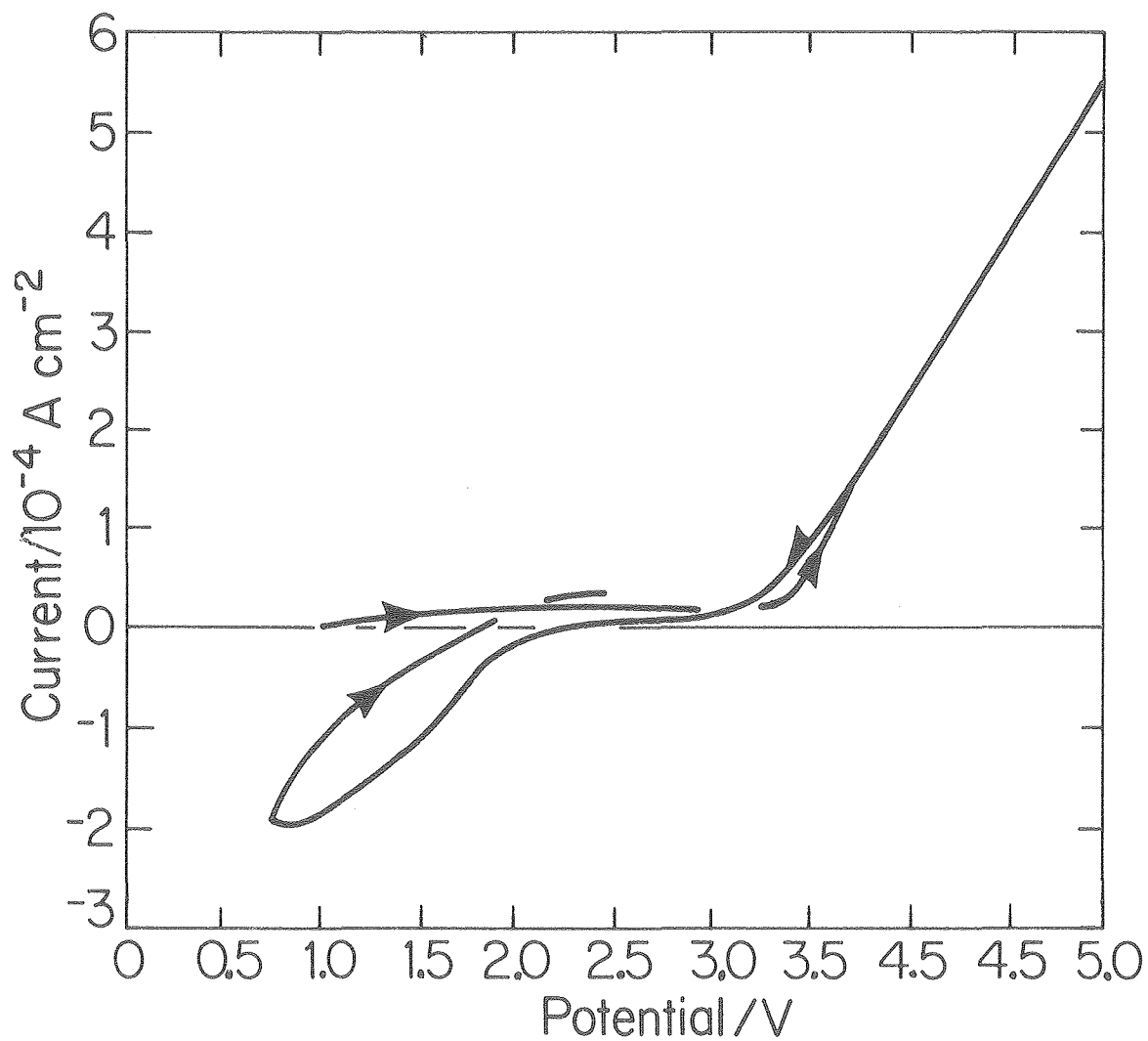
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Figure 10. Cyclic voltammogram of potassium deposition in 0.5 M KAlCl$_4$/PC
@ 25°C using cell #2. The sweep rate is 200 mv/sec. and the
CE, WE and RE are respectively platinum, stainless steel and
potassium.

Table 6. Analytical Results for Electrochemical Cl_2 Evolution in Cell #2

	Initial	Cl_2 bubbling <1 min	Cl_2 bubbling 2 hrs	After 10 ppm water was injected
Propylene oxide	0	463	10^5	2×10^5
Propylene glycol	<5	507	10^5	2×10^5
Allyl alcohol	0	98	2×10^3	3×10^3
Acetone/Propionaldehyde	0	230	2×10^3	2×10^3
Water	<3	--	<3	~10

counter electrodes using potassium as the reference electrode. Current density was estimated to be 80 $\mu a/cm^2$ and stayed pretty much constant throughout the experiment. The solution in the anodic chamber slowly turned greenish yellow while that in the cathode chamber remained color-less. Electrolysis was conducted for more than 12 hours. Traces of potassium deposits were observed. Samples from both chambers were taken for GC analysis at <1 minute, 2 hours and 12 hours after initiation of electrolysis. The results are recorded in Table 7.

Judging from these results, degradation was confined only to the anodic chamber. The initial degradation rate was slow probably due to the slower rate of chlorine formation. However, the overall extent of de-gradation was similar to the results obtained in electrolysis using cell #2. This leads us to suspect that the extent of degradation is a strong function of the amount of water present in the solvent. Since the degradation was confined only to the anodic chamber, future work will involve making provisions to continuously withdraw anodic solution for purification.

Table 7. Analytical Result of In-situ Cl_2 Evolution Using Cell #3

I. Cathodic solution

	(ppm)	
	Initial	End of expt. (12 hr)
Propylene oxide	0	0
Propylene glycol	<5	<5
Allyl alcohol	0	0
Acetone/Propionaldehyde	0	0
Water	<3	<3

II. Anodic solution

	(ppm)			
	Initial	<1 min	2 hr	> 2 hr
Propylene oxide	0	25	2×10^4	5×10^4
Propylene glycol	<5	150	2×10^4	5×10^4
Allyl alcohol	0	<10	0.5×10^3	10^3
Acetone/Propionaldehyde	0	∿30	10^3	10^3
Water	<3	–	<3	<3

CONCLUSIONS

The foregoing study on the stability of propylene carbonate with respect to halogen evolution, specifically chlorine, has led to the following conclusions:

(1) The feasibility of cathodic potassium deposition with simultaneous anodic chlorine evolution in a 0.5M $KAlCl_4$/PC electrolytic medium was established.

(2) Chlorine was found to degrade even the most carefully prepared/ purified propylene carbonate solvent which contains <2 ppm and <5 ppm of water, and propylene glycol, respectively.

(3) Water was proven to play a key role in the degradation process. It not only affects the rate but also the extent of the degradation. A rough estimate reveals that 10 ppm of water has caused both the rate and extent of the degradation to increase by as much as tenfold.

(4) Treated Nafion membrane was found to be adequate to confine degradation to only the anodic chamber where chlorine was continuously evolved during electrolysis.

(5) The chlorine evolution potential of a 0.5M $KAlCl_4$ in propylene carbonate was determined by voltammetry to be 3.5 volts, relative to potassium metal.

Acknowledgment

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